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GEORGIA INSTITUTE OF TECHNOLOGY
OFFICE OF CONTRACT ADMINISTRATION
SPONSORED PROJECT INITIATION

Date: December 9, 1976

Project Title: Reactivity of Biphenyl in Carpet Processing Wastes

Project No: E-27-650

Project Director: Dr. W. C. Tincher

Sponsor: The Carpet and Rug Institute

Agreement Period: From 11/3/76 Until 3/2/77

Type Agreement: Standard Industrial Research Agreement, dated 11/3/76

Amount: $7,228

Reports Required: Monthly Reports; Final Report

Sponsor Contact Person (s):

Technical Matters

Contractual Matters (thru OCA)

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Defense Priority Rating: None

Assigned to: Textile Engineering (School/Laboratory)

COPIES TO:

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- Project Code (GTRI)
- Other

CA-3 (3/76)

GEORGIA INSTITUTE OF TECHNOLOGY
OFFICE OF CONTRACT ADMINISTRATION

SPONSORED PROJECT TERMINATION

no action

Date: 4/12/78

Project Title: Reactivity of Biphenyl in Carpet Processing Wastes

Project No: E-27-650 (Sub-Project is E-20-608/Gould/CE)

Project Director: Dr. Tincher

Sponsor: The Carpet and Rug Institute

Effective Termination Date: 6/30/77

Clearance of Accounting Charges: 6/30/77

Grant/Contract Closeout Actions Remaining:

X Final Invoice and Closing Documents

_ Final Fiscal Report

_ Final Report of Inventions

_ Govt. Property Inventory & Related Certificate

_ Classified Material Certificate

_ Other _____

NOTE: This termination sheet terminates E-27-650 and sub-project E-20-608.

Assigned to: TE (CE) (School/Laboratory)

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- Project Code (GTRI)
- Other Dr. J.P. Gould/CE
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CA—4 (3/76)

Reactivity of Biphenyl in Carpet Processing Wastes

by

Wayne C. Tincher
School of Textile Engineering

and

Joseph P. Gould
School of Civil Engineering

Prepared Under Contract No.
E-27-650

for

Carpet and Rug Institute
Dalton, Georgia 30720

Georgia Institute of Technology
Atlanta, Georgia 30332

September, 1977

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ABSTRACT

Biphenyl is a common component in carriers used in dyeing polyester carpet. There is some concern that biphenyl may react with chlorine either during carpet processing or in treatment of carpet dyeing waste to produce chlorinated biphenyls. This work was undertaken to determine if chlorination of biphenyl can occur under conditions likely to be encountered in carpet production and waste treatment.

Samples were collected from the Dalton water supply and at various points in the Dalton waste treatment plant and analyzed for chlorinated biphenyls. In addition, solutions of biphenyl were subjected to chlorine under a variety of conditions in the laboratory to simulate conditions which occur in carpet processing and dye waste treatment. These samples were analyzed also for chlorinated biphenyls.

All samples were analyzed by gas chromatography. Chlorinated biphenyls were identified by comparison of retention times of peaks in the samples with retention times of known chlorinated biphenyl compounds and commercial mixtures of chlorinated biphenyls (Aroclors). Coincidence of peak positions on at least two different chromatography columns was considered strong evidence for the presence of a particular chlorinated biphenyl isomer. The quantity of each identified chlorinated biphenyl compound was determined from the area under the gas chromatography peak compared to the area for a known quantity of the standard compound.

Based on the results a number of conclusion are possible. First, There is no evidence from either the samples collected at the Dalton waste treatment plant or the laboratory chlorination experiments that poly-

chlorinated biphenyls are produced under conditions that usually exist in treating carpet dye wastewater. Second, chlorinated biphenyls are entering the Dalton waste treatment plant from some source within the city. These compounds are not present in the water supply but are present in the influent to the waste treatment plant. Laboratory chlorination experiments indicate that some chlorinated biphenyls may be produced when polyester carpet is stripped with chlorine containing stripping agents. Stripping of carpet with these agents and the use of sodium hypochlorite (bleach) and other chlorinating agents should be discouraged if the spent baths contact biphenyl, particularly under acidic conditions.

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I. Introduction

Biphenyl is a common constituent in many "carrier" formulations used in the dyeing of polyester carpet. It is estimated that in 1974 4 - 5 million pounds of biphenyl were used by the carpet industry[1]. Biphenyl itself does not present major problems from a toxicity[2] or tumorigenicity standpoint[3]. Considerable concern has been expressed about possible harmful effects of polychlorinated biphenyl[4] in the environment. Commercial polychlorinated biphenyls or PCB's are mixtures of highly chlorinated biphenyls and are used principally as heat transfer liquids in electrical equipment. The Monsanto Company has been the major manufacturer of polychlorinated biphenyls in the United States and has marketed a number of mixtures under the "Aroclor" tradename.

In the past few years there has been some concern that biphenyl present in carpet dyeing processes and in carpet dyeing wastes may be converted to chlorinated biphenyls. The highly chlorinated compounds usually designated PCB's are not expected to be produced in aqueous chlorination of biphenyl. It was considered possible that some mono- and/or dichloro- substituted biphenyl may be produced under typical conditions existing carpet dyeing and wastewater treatment. Gaffney[5] reported finding polychlorinated biphenyls in a sewage treatment plant having a high influx of textile dyeing waste and suggested chlorination of the textile waste as a possible source for the polychlorinated biphenyls. However, the treatment plant studied by Gaffney also receives waste from a transformer plant known to have been using polychlorinated biphenyls at the time of the Gaffney study.

Carlson and coworkers[6] have reported that biphenyl can be chlorinated under certain conditions to give a variety of mono- and dichloro- derivatives at the parts-per-billion level. Unfortunately, none of the conditions

studied by Carlson approximate the conditions which are likely to be experienced by carpet dye waste in chlorination processes in waste treatment plants or in disinfection processes in water treatment plants.

Johnsen[7] has reported the presence of chlorinated biphenyls in chlorinated aqueous solutions of biphenyl but no quantitative data were given.

The possibility of chlorination of biphenyl was investigated briefly in the Georgia Tech laboratories[8] and no evidence of chlorination was found. However, the analytical techniques available at the time of this earlier study were not sufficiently sensitive to detect chlorinated biphenyls at the parts-per-billion level.

The present work was undertaken to determine to what extent chlorinated biphenyls may be produced under conditions likely to occur during carpet processing and in the treatment of carpet processing wastes.

II. Plan of the Study

In planning the study three types of samples were selected for investigation. First, samples were collected at the Dalton, Georgia, water treatment and waste treatment plants. The samples at the water treatment plant were selected for study to ensure that results would not be confused by chlorinated compounds present in the water supply. Samples were collected at the waste treatment plant both before and after chlorination to determine what effect typical chlorination procedures would have on carpet processing wastes (approximately 75% of the wastewater treated at the Dalton plant is carpet processing waste). A sample was also taken from the Conasauga River just below the outfall of the Dalton waste treatment plant.

A second set of samples was prepared by chlorination of a saturated solution of biphenyl in water under a variety of conditions. Conditions

were selected to reproduce studies already reported in the literature and to simulate typical conditions in treating of textile waste.

A third part of the study was directed toward determining whether biphenyl is chlorinated under some conditions of carpet processing. In the stripping (removal of dye) from polyester carpet, biphenyl may come in contact with chlorine containing compounds under conditions of low pH. This condition was simulated in the laboratory and the stripping wastewater analyzed for chlorinated biphenyls.

It was expected that mono-, di-, and trichlorobiphenyl isomers would predominate in samples containing biphenyl exposed to the cholorination conditions investigated in this study. Major effort was directed therefore, to identification and quantitation of these isomers.

Gas chromatography was selected for separation and quantitative analysis of the various chlorinated biphenyls. Pure samples of chlorinated biphenyl and commercial mixtures of chlorinated biphenyl were run under the same conditions as the samples to assist in identification and quantitation of the various isomers. Identification was considered positive if pure compound and sample peak retention times were the same on two different gas chromatography columns. Additional efforts to confirm gas chromatography peak assignments by mass spectral analysis were attempted but these attempts were not successful.

With the analytical procedures available, chlorinated biphenyls could be detected in the various wastewater samples at concentrations less than 1 part-per-billion.

III. Experimental Details

A. Samples

The samples investigated in this study are listed in Table 1. All samples were grab samples collected in new 1 gallon glass bottles equipped with teflon lined caps. The bottles were carefully washed in Micron detergent, rinsed with distilled water, rinsed with Fisher pesticide grade acetone, extracted 3 times with Fisher pesticide grade hexane, and dried. Water treatment plant, waste treatment plant and stream samples were refrigerated immediately upon collection and remained at 0°C until extracted. The laboratory chlorinated samples were not refigerated since the chlorination treatments were expected to prevent microbial degradation.

The city of Dalton uses water from both Mill Creek and the Conasauga River. Raw and finish water from both water treatment plants were included in the study.

Wastewater samples were taken at the new Dalton waste treatment plant on River Bend Road. The influent sample was taken at the bar screen when the flow at the treatment plant was at near maximum. This should correspond to the time at which the plant is receiving the maximum quantity of carpet dye waste. Flow at the time of collection was approximately 34 million gallons per day.

The clarifier effluent sample was taken from both of the clarifiers, Since the residence time in the activated sludge system is approximately 24 hours, the clarifier sample contains wastewater that was entering the plant the previous day. The activated sludge sample was collected from each of the two return activated sludge pumps.

Table 1

Samples Analyzed for Chlorinated Biphenyls

Notebook Reference	Sample Description	Collection Time	
129-10-1	Dalton Finish Water (Conasauga)	10/28/76	11:15 AM
129-10-2	Dalton Raw Water (Conasauga)	10/28/76	11:45 AM
129-10-3	Dalton Finish Water (Mill Creek)	10/28/76	1:45 PM
129-10-4	Dalton Raw Water (Mill Creek)	10/28/76	2:10 PM
129-11-5	Dalton Waste Treatment Plant Influent (Bar Screen)	10/28/76	3:15 PM
129-11-6	Dalton Waste Treatment Plant Clarifier Effluent	10/28/76	3:45 PM
129-11-7	Dalton Waste Treatment Plant Return Activated Sludge	10/28/76	4:15 PM
129-11-8	Dalton Waste Treatment Plant Effluent	10/28/76	5:00 PM
129-12-9	Conasauga River at Looper's Bridge	10/28/76	5:15 PM
129-19-1	Saturated Biphenyl Solution; NaOCl (10 mg/l Cl_2), pH = 7.2, 60 min		
129-19-2	Saturated Biphenyl Solution; Cl_2, 260 mg/l, pH = 6.0, 10 min.		
129-19-3	Saturated Biphenyl Solution; Cl_2, 2,300 mg/l, pH = 2.2, 15 min.		
129-19-4	Saturated Biphenyl Solution (Control)		
129-25-1	Saturated Biphenyl Solution; Cl_2 10 mg/l, pH = 6.0, 60 min.		
NB 149-3/1/77	Wastewater from Simulated Chlorite Strip		

The effluent sample was collected at the point where the waste treatment plant effluent enters Drowning Bear Creek. This is immediately after the contact chlorination unit. The Dalton plant normal chlorine dose rate is 1500 to 2000 pounds of chlorine per 32 million gallons of water. The rate at the time of sample collection was 1450 pounds of chlorine per day. The pH during chlorination was 6.4 - 6.8 [9]. Sampling points are shown in Fig. 6.

A sample was also collected from the Conasauga River at Looper's Bridge. This site is approximately 1 river mile below the outfall of Drowning Bear Creek. The sample was taken from the Whitfield County side of the Conasauga since complete mixing of the Dalton waste treatment plant effluent and the Conasauga River has not occurred at this point and the effluent concentration is higher on the Whitfield County side.

In addition to the stream samples, several samples were prepared in the laboratory by chlorination of a saturated biphenyl solution. Five gallons of this solution were prepared by placing biphenyl (Eastman) in high purity distilled water and allowing the solution to stand for 40 hours. Under these conditions the water should contain 5 to 7 parts-per-million of biphenyl. One gallon samples of this solution were then subjected to a variety of chlorination conditions.

Sample 129-19-1 was buffered at a pH of 7.2 with a phosphate buffer solution and treated at 23°C with sodium hypochlorite (NaOCl) solution to a level of 10 mg/l chlorine. The contact time was 1 hour after which the solution was dechlorinated with sodium bisulfite to negative on starch-iodide test paper. These conditions were designed to simulate chlorination of wastewater in a typical waste treatment plant.

Sample 129-19-2 was an attempt to simulate conditions that might be encountered in decolorization of dye waste with chlorine gas. One gallon of the biphenyl solution was buffered at 7.0 with phosphate and chlorine gas added at 90 mg/min. for approximately 10 minutes. The total dose was 260 mg/1, and the residual chlorine after treatment was 175 mg/1 and the final pH was 6.0. Some sodium hydroxide was added midway during the treatment to prevent further lowering of the pH. The treatment temperature was approximately 35°C and the sample was dechlorinated after treatment with sodium bisulfite.

Sample 129-19-3 was an attempt to simulate work previously reported by Carlson [6]. Chlorine gas was added to the saturated biphenyl solution at a rate of 300 mg/min for 30 min. for a total dose of approximately 2,300 mg/1. The final residual chlorine concentration was 1,275 mg/1. No buffering was used in this experiment so the pH fell from an initial value of 6.4 to 2.1. The temperature was 23°C and after a 15 min. contact period following chlorination the sample was dechlorinated with sodium bisulfite. Since it has been reported that significant quantities of chlorinated biphenyls are produced under these conditions [6], it was felt that this sample would serve as a check on the chlorination procedures and analytical methods.

Sample 129-19-4 was a sample of the saturated biphenyl solution used as a control for the experiment.

Sample 129-25-1 was a second simulation of waste treatment plant chlorination conditions. This sample was treated for 60 minutes with chlorine gas at a concentration of 10 mg/1. The pH was 6.0 for this experiment.

Sample NB 149-3/1/77 was a laboratory simulation of a typical polyester carpet stripping process. Occasionally a carpet will be too dark in color at the end of the dyeing cycle and the dye must be removed so that the carpet can be redyed. Sodium chlorite is frequently used as a dye oxidizing agent in these stripping operations. A typical stripping recipe is shown below (all percentages are based on weight of fiber in the carpet):

2% surfactant

2% formic acid (pH 3.5)

10% biphenyl based carrier

6% sodium chlorite

The sample is treated in the solution at 100°C for 1 hour and then rinsed in 2% sodium bisulfite. Sample NB-149 was the residual stripping bath used in this type of treatment.

B. Analysis of Samples

Gas chromatograph (GC) was used for identification and for quantitative analysis of components present in the various samples. The time that a chemical compound is retained on a GC column at a particular temperature in the presence of flowing carrier gas is characteristic of the compound. Compounds can be identified by comparing retention times of known compounds (under carefully controlled conditions of temperature and carrier gas flow rate) with retention times of compounds present in unknown samples. Generally, if the retention times of an unknown compound are identical to the retention times of a known compound on two different columns, a positive identification is assumed. Quantities of identified components are determined by comparing the area under the GC peak of the component

with the area obtained from a known compound at a known concentration.

Gas chromatograms were run by Southeast Laboratories, Inc., Atlanta, Georgia. The instrument employed was a Hewlett-Packard Model 5830A equipped with a Nickel 63 electron capture detector. This detector is especially sensitive to compounds containing electronegative elements such as chlorine. Three different colums (6' x 1/4" id glass) were used during the course of the work -- approximately 6% OV-17 on Chromosorb WHP, 8% OV-17 on Chromosorb WHP, and 3% OV-1 on Chromosorb WHP. Conditions of the various runs are shown in Table 2.

The conditions were selected to give good separations of the mono-, di-, and trichlorobiphenyl isomers which were of major interest in the study.

The retention times of various components in the samples investigated were determined relative to pp'DDE under the same conditions by the equation [10,11]

$$RRT = \frac{\text{Retention time} \times 100}{\text{Retention time of pp'DDE}}$$

Areas of peaks were determined directly by the integration system of the Hewlett Packard instrument.

Standard samples of several Aroclors (Aroclor 1221, Aroclor 1242, Aroclor 1248, Aroclor 1254) which are commercial mixtures of chlorinated biphenyls and pure mono-, di-, and trichlorobiphenyls were obtained from Analabs, Inc. These standards were injected in the gas chromatograph under the same conditions as the wastewater samples. The relative retention times of the standard materials were determined and used to identify possible chlorinated biphenyl in the wastewater and lab chlorinated samples. The areas under the observed peaks in chromatograms of the

Table 2

Conditions for Gas Chromatographic Analyses

Column	6% OV-17	%8 OV-17	3% OV-1
Column Temp.	200°C	220°C	200°C
Injector Temp.	225°C	225°C	225°C
Detector Temp.	250°C	250°C	250°C
Flow	69 ml/min	70 ml/min	70 ml/min
Sample Size	~ 2 ul	~2 ul	~2 ul

standard samples were also used to determine the sensitivity of the detector and to quantitate suspected chlorinated biphenyls in the samples.

Typical chromatograms of Aroclor 1222 and Aroclor 1242 on the 6% OV-17 column are shown in Figure 1. These chromatograms indicate the separations of the mono-, di- and trichlorobiphenyl isomers achieved under the conditions given in Table 2. Chromatograms of samples are shown in Figures 2-5.

Table 3 gives the retention time and retention time relative to pp'DDE (Retention Time = 29.05) of peaks in the gas chromatograms of Aroclors 1221, 1242, 1248, and 1254. The relative retention times reported by Webb and McCall [10] are shown for comparison. Peak positions for the various mono-, di- and trichlorobiphenyl isomers are also given. The model compound retention times shown in parentheses are calculated values. They were obtained in a series of experiments for which the retention time of pp'DDE was 27.67 and the compound retention times have been calculated based on a pp'DDE retention time of 29.05 minutes.

Similar data are shown in Table 4 for gas chromatography runs with the 3% OV-1 column. On this column the retention time of pp'DDE was 11.13 minutes. Peak positions for chlorinated biphenyls on the 8% OV-17 column are given in Table 5.

Table 6 gives the retention times of peaks, retention times relative to pp'DDE, and area of peaks present in gas chromatograms of samples of raw and finish water from the two sources used by the city of Dalton. Samples 129-10-1, 129-10-2, 129-10-3, and 129-10-4 were also run on the 8% OV-17 column at 225°C. These samples were analyzed to determine if any chlorinated biphenyls were present in water being used by the city of Dalton. Peak positions and areas for the 8% OV-17 column are given in Table 7.

Table 3

Retention Times of Chlorinated Biphenyls on 6% OV-17
(pp'DDE = 29.05)

Compound	Retention Time	Aroclor 1221	Aroclor 1242	Aroclor 1248	Aroclor 1254	Average Retention Time	Relative Retention Time	Webb & McCall R.R.T.
2-Monochloro-	2.93	2.93	2.95	-	-	2.94	10	11
3-Monochloro-	(3.66)	-	-	-	-	3.66	13	-
4-Monochloro-	3.91	3.91	-	-	-	3.91	13	14
2,6-Dichloro-	(4.32)	-	-	-	-	4.32	15	-
2,2'-Dichloro-	4.50	4.44	4.48	-	-	4.47	15	16
2,5-Dichloro	(4.87)	-	-	-	-	4.87	17	19
2,4-Dichloro-	4.96	4.96	4.96	-	-	4.96	17	-
2,3-Dichloro-	(5.77)	5.78	5.78	5.79	-	5.78	20	21
2,4,6-Trichloro-	(6.38)	6.88	6.88	-	-	6.88	24	-
3,3'-Dichloro-	(7.09)	-	-	-	-	7.09	24	-
3,4-Dichloro-	(7.44)	-	-	-	-	7.44	26	-
—	-	7.58	7.60	7.60	-	7.59	26	28
—	-	9.00	9.02	9.01	-	9.01	31	32
2,4,4'-Trichloro-	(10.17)	10.28	10.30	10.29	-	10.26	35	37
—	-	11.28	11.32	11.33	-	11.31	39	40
—	-	12.98	13.04	13.04	12.97	13.01	45	47
—	-	15.68	15.62	15.65	15.63	15.66	54	54
—	-	-	16.84	16.85	16.75	16.81	58	58
—	-	-	18.96	19.07	-	19.02	65	-
—	-	-	20.46	20.61	20.59	20.55	71	70
—	-	-	-	23.28	23.37	23.33	80	84
—	-	-	-	29.52	29.82	29.67	102	104
—	-	-	-	31.90	32.01	31.96	110	112
—	-	-	-	-	36.75	36.75	126	125
—	-	-	-	-	38.42	38.42	132	-
—	-	-	-	-	41.50	41.50	143	146
—	-	-	-	-	46.99	46.99	162	160
—	-	-	-	-	54.03	54.03	186	174
—	-	-	-	-	56.53	56.53	195	-

Table 4

Retention Times of Chlorinated Biphenyls on 3% OV-1
(pp'DDE = 11.13)

Compund	Standard Retention Time	Aroclor 1221	Aroclor 1242	Aroclor 1248	Aroclor 1254	Average Retention Time	Relative Retention Time	Webb & Mccall R.R.T.
2-monochloro-	1.55	1.54	-	-	-	1.54	14	11
4-monochloro-	1.93	1.95	-	-	-	1.94	18	14
2,2'-dichloro-	2.13	2.11	2.13	2.13	-	2.13	19	16
—	-	2.45	2.47	-	-	2.46	22	19
—	-	2.67	2.69	2.69	-	2.68	24	21
—	-	-	2.96	2.97	-	2.97	27	-
—	-	3.39	3.41	3.40	-	3.40	31	28
—	-	3.76	3.77	3.77	3.68	3.75	34	32
—	-	4.49	4.50	-	-	4.50	40	37
—	-	4.69	4.73	4.72	4.70	4.71	42	40
—	-	-	-	5.02	-	5.02	45	-
—	-	5.55	5.55	5.56	5.48	5.54	50	47
—	-	6.16	6.17	6.18	6.16	6.17	55	54
—	-	6.64	6.69	6.64	6.64	6.64	60	58
—	-	8.08	8.08	8.06	8.06	8.07	73	70
—	-	-	9.14	9.31	9.52	9.32	84	84
—	-	-	10.99	11.00	-	11.00	99	98
—	-	-	11.73	11.68	11.70	11.70	105	104
—	-	-	-	-	13.92	13.92	125	125
—	-	-	-	16.27	16.44	16.36	147	146
—	-	-	-	17.25	17.61	17.43	157	160
—	-	-	-	19.31	19.44	19.38	174	174
—	-	-	19.71	19.76	-	19.76	176	-
—	-	-	-	26.19	-	26.19	235	-
—	-	-	-	29.47	29.44	29.46	265	-

Table 5

Retention Times of Chlorinated Biphenyls on 8% OV-17
(pp'DDE = 36.76)

Compound	Standard Retention Time	Aroclor 1221 Retention Time	Aroclor 1248 Retention Time	Aroclor 1254 Retention Time	Average Retention Time	Relative Retention Time	Webb & McCall R.R.T.
2-Monochloro-	-	3.91	-	-	3.91	11	11
3-Monochloro-	4.97	-	-	-	4.97	14	-
4-Monochloro-	5.15	5.01	-	-	5.08	14	14
2,6-Dichloro-	6.19	-	-	-	6.19	17	-
2,2'-Dichloro-	6.27	6.02	-	-	6.15	17	16
2,4-Dichloro-	6.81	6.55	-	-	6.68	18	-
2,5-Dichloro-	6.81	-	-	-	6.81	19	-
2,3-Dichloro-	8.10	-	7.69	-	7.90	21	21
2,4,6-Trichloro-	8.97	-	-	-	8.97	24	-
3,3'-Dichloro-	9.57	-	-	-	9.57	26	-
3,4-Dichloro-	10.13	-	-	-	10.13	28	-
4,4'-Dichloro-	10.67	10.06	10.20	-	10.31	28	28
2,4,4'-Trichloro-	13.73	13.19	13.37	13.49	13.45	37	37
—	-	-	14.73	-	14.73	41	40
—	-	-	15.94	-	15.94	43	-
—	-	-	17.01	16.90	16.96	46	47
—	-	-	20.37	20.35	20.36	56	54
—	-	-	22.05	22.17	22.11	60	58
—	-	-	25.41	25.30	25.36	69	70
—	-	-	27.37	-	27.37	74	78
—	-	-	30.31	30.20	30.26	82	84
—	-	-	-	32.49	37.49	88	-
—	-	-	40.25	40.19	40.22	109	-
—	-	-	45.51	45.96	45.74	124	125
—	-	-	-	50.92	50.92	139	146
—	-	-	-	54.24	54.24	148	160
—	-	-	-	58.32	58.32	159	174
—	-	-	-	62.05	62.05	169	-
—	-	-	-	65.77	65.77	179	203
—	-	-	-	84.69	84.69	230	232

Table 6

Gas Chromatogram Peaks for Raw and Finish Water Samples on 3% OV-1

Sample 129-10-1 Dalton Finish Water (Conasauga)		Sample 129-10-2 Dalton Raw Water (Conasauga)		Sample 129-10-3 Dalton Finish Water (Mill Creek)		Sample 129-10-4 Dalton Raw Water (Mill Creek)		Average Relative Retention
Peak R.T.	Area	Peak R.T.	Area	Peak R.T.	Area	Peak RT	Area	Time
2.61	61.2	2.59	14.4	2.61	140.9	2.61	28.5	23
2.85	0.6	-	-	-	-	-	-	26
3.41	1.3	-	-	-	-	-	-	31
-	-	3.78	1.1	-	-	-	-	34
4.47	0.5	4.46	0.5	4.52	12.5	4.51	-	40
5.03	6.0	5.02	5.5	5.07	2.8	4.07	2.2	46
5.43	4.0	5.47	9.9	-	-	5.51	8.3	49
6.03	1.8	-	-	-	-	-	-	54
-	-	6.86	7.8	-	-	-	-	62
8.75	2.3	8.74	2.2	-	-	8.83	1.1	79
9.72	1.3	9.69	2.6	-	-	-	-	87
10.24	1.4	-	-	-	-	-	-	92

Table 7

Gas Chromatograph Peaks For Raw and Finish Water Samples on 8% OV-17

Sample 129-10-1 Dalton Finish Water (Conasauga)		Sample 129-10-2 Dalton Raw Water (Conasauga)		Sample 129-10-3 Dalton Finish Water (Mill Creek)		Sample 129-10-4 Dalton Raw Water (Mill Creek)		Average Relative Retention Time
Peak R.T.	Area	Peak R.T.	Area	Peak R.T.	Area	Peak R.T.	Area	
4.38	21.0	4.40	-	-	-	4.42	-	12
-	-	4.94	0.5	-	-	-	-	13
-	-	5.52	0.6	-	-	-	-	15
-	-	-	-	-	-	-	-	16
-	-	6.20	1.5	6.38	0.5	-	-	17
-	-	-	-	-	-	-	-	18
8.06	0.9	7.97	1.4	7.97	-	7.94	0.5	22
-	-	-	-	-	-	-	-	25
9.78	2.3	-	-	-	-	-	-	27
10.38	0.5	-	-	10.17	0.7	-	-	28
10.90	1.5	10.89	3.0	10.83	1.0	10.83	1.8	30
11.98	2.1	11.93	2.1	11.99	0.5	11.74	0.9	32
13.50	16.5	13.41	14.8	13.44	9.4	13.34	8.0	37
-	-	-	-	14.33	1.2	-	-	39
16.50	4.0	16.37	10.3	16.43	5.2	16.27	6.4	45
18.65	1.3	18.69	1.0	-	-	18.47	4.5	51
20.42	2.0	20.37	3.1	20.13	5.2	20.43	-	55
-	-	-	-	-	-	21.94	1.5	59
23.97	1.0	24.07	1.1	23.93	1.1	-	-	65
27.51	7.5	27.37	15.9	27.47	5.5	27.39	6.6	75
-	-	-	-	-	-	-	-	78
30.03	1.9	29.93	2.8	29.99	1.5	30.06	0.9	82

Comparison of the data in Tables 6 and 7 with positions of the chlorinated biphenyls in Tables 4 and 5 suggest that peaks near 2.60 (RRT = 23) on the OV-1 column corresponding to peaks near 8.0 on the 8% OV-17 (RRT = 22) are probably due to 2,3- or 2,5-dichlorobiphenyl (RRT = 21 in the paper by Webb and McCall). Similarly, the peak with retention times near 4.50 on the OV-1 column (RRT = 40) and near 13.45 on the OV-17 column (RRT = 37) are probably due to 2,4,4'-trichlorobiphenyl (RRT = 37 in Webb and McCall). There is also the possibility of 4-monochlorobiphenyl (RRT = 14) and 2,2' dichlorobiphenyl being present in the water samples but this could not be confirmed due to the high background observed at short retention times on the OV-1 column. A summary of the chlorinated biphenyls present in the water samples is given in Table 8.

Retention times for peaks observed in the chromatograms of samples collected at the Dalton waste treatment plant and from the Conasauga River below Dalton are given in Tables 9, 10, and 11. Comparison of relative retention times with relative retention times of the standard samples (Tables 4,5 and 6) suggest that 2-monchloro-, 2,2,'-dichloro-, 2,4-dichloro-, 2,3-dichloro-, and 2,4,6-trichlorobiphenyl are present in the samples analyzed. The relative retention times and areas are shown in Table 12.

Peaks in the gas chromatograms of the laboratory chlorinated biphenyl solutions on the 6% OV-17 column are given in Table 13 and on the 8% OV-17 column in Table 14. Comparison of the peak positions with the standard compounds shown in Tables 3 and 5 suggest that the following chlorinated biphenyls are present:

Table 8

Chlorinated Biphenyls Present in Dalton Water Samples

3% OV-1

Compound	R.R.T. Webb & McCall	R.R.T. this work	RAW WATER(C) 129-10-2 RRT	RAW WATER(C) 129-10-2 Area	FINISH WATER(C) 129-10-1 RRT	FINISH WATER(C) 129-10-1 Area	RAW WATER(M) 129-10-4 RRT	RAW WATER(M) 129-10-4 Area	FINISH WATER(M) 129-10-3 RRT	FINISH WATER(M) 129-10-3 Area
4-monchloro-	14	18	-	-	-	-	-	-	-	-
2,2'-dichloro-	16	19	-	-	-	-	-	-	-	-
2,3- and 2,5-dichloro	21	24	23	14.4	23	61.2	23	28.5	23	140.9
2,4,4'-trichloro	37	40	40	0.5	40	0.5	41	-	41	12.5

8% OV-17

Compound	R.R.T. Webb & McCall	R.R.T. this work	RAW WATER(C) 129-10-2 RRT	RAW WATER(C) 129-10-2 Area	FINISH WATER(C) 129-10-1 RRT	FINISH WATER(C) 129-10-1 Area	RAW WATER(C) 129-10-4 RRT	RAW WATER(C) 129-10-4 Area	FINISH WATER(C) 129-10-3 RRT	FINISH WATER(C) 129-10-3 Area
4-monochloro-	14	14	13	0.5	-	-	-	-	-	-
2,2'dichloro-	16	17	17	1.5	-	-	-	-	17	0.5
2,3- and 2,5-dichloro-	21	21	22	1.4	22	0.9	22	0.5	22	-
2,4,4'-trichloro-	37	37	37	14.8	37	16.5	37	8.0	37	9.4

Table 9

Peaks in Chromatograms of Dalton Waste Treatment Plant
and Conasauga River Samples on 3% OV-1

PLANT INFLUENT 129 11-5		CLARIFIER EFFLUENT 129-11-6		RETURN SLUDGE 129-11-7		PLANT EFFLUENT 129-11-8		LOOPER'S BRIDGE 129-11-9	
Retention Time	Area	Retention Time	Area	Retention Time	Area	Retention Time	Area	Retention Time	Area
1.17	22.4	1.16	3.0	1.19	24.5	1.17	39.1	1.17	0.8
1.37	116.6	1.35	84.7	1.37	37.1	1.37	98.5	1.36	11.1
-	-	1.58	22.1	1.59	8.6	1.60	75.8	1.58	2.3
-	-	-	-	1.75	20.8	-	-	-	-
-	-	2.16	190.1	2.17	203.7	2.22	271.8	2.16	12.9
2.94	13,400.0	2.93	315.0	2.95	332.6	2.95	270.3	2.91	17.2
-	-	3.91	109.2	3.94	94.0	3.91	51.3	4.05	10.8
-	-	-	-	4.45	5.6	-	-	4.75	-
-	-	5.04	10.8	5.09	7.6	5.06	0.9	5.03	3.2
-	-	5.50	10.0	5.45	9.4	5.52	21.6	5.45	2.8
5.78	986.6	5.74	13.8	5.79	20.1	*	-	-	-
-	-	6.45	7.8	6.47	1.0	6.47	9.7	6.45	1.1
6.84	345.0	-	-	-	-	-	-	-	-
-	-	7.51	82.5	7.56	192.5	7.52	98.7	-	-
-	-	*	-	*	-	*	-	8.75	2.2
-	-	9.57	6.2	9.64	31.6	9.63	6.4	9.65	0.8
10.61	479.5	10.49	7.8	10.54	39.9	10.51	8.5	*	-
11.91	42.6	11.87	481.0	11.88	551.9	11.88	479.8	11.87	30.6
16.93	53.4	16.87	168.4	16.89	50.2	16.88	183.7	16.93	33.9
-	-	-	-	*	-	19.20	20.5	-	-
-	-	-	-	*	-	20.15	1.8	-	-
22.77	0.6	22.73	5.2	22.78	17.8	22.72	2.0	-	-

* Peak Detected

Table 10

Peaks in Chromatograms of Dalton Waste Treatment Plant and Conasauga River Samples on 6% OV-17 (pp'DDE = 29.05)

PLANT INFLUENT 129-11-5		CLARIFIER EFFLUENT 129-11-6		RETURN SLUDGE 129-11-7		PLANT EFFLUENT 129-11-8	
Retention Time	Area	Retention Time	Area	Retention Time	Area	Retention Time	Area
1.15	2965.0	1.14	273.3	1.15	291.4	1.16	242.9
1.31	7088.0	1.29	654.8	1.31	257.9	1.31	1155.0
2.07	190.3	2.05	102.8	2.07	150.9	2.07	142.3
-	-	*	-	2.44	62.4	2.40	13.6
*	-	2.93	12.7	2.96	66.1	2.96	67.9
3.25	8.1	*	-	*	-	*	-
-	-	3.39	6.4	3.29	87.5	3.35	31.7
3.52	19.3	*	-	*	-	*	-
-	-	-	-	-	-	4.17	43.3
4.43	89.8	4.55	22.2	*	-	*	-
5.05	567.5	4.95	161.3	4.97	238.4	4.95	117.6
-	-	5.70	26.3	*	-	5.69	91.8
6.02	146.2	6.06	115.3	6.07	370.0	6.07	177.4
6.82	177.0	6.63	41.9	*	-	*	-
8.97	41.2	*	-	*	-	*	-
*	-	9.27	120.8	*	-	9.29	76.8
11.77	404.8	*	-	11.24	408.3	*	-
11.78	180.7	-	-	-	-	-	-
12.47	26.6	-	-	-	-	-	-
13.43	120.5	13.40	47.4	13.32	288.1	13.41	31.8
-	-	14.32	6.9	-	-	-	-
-	-	15.05	6.7	-	-	15.14	1.7
21.10	946.0	21.20	27.5	21.08	96.2	21.21	31.2
-	-	-	-	-	-	22.69	6.5
24.97	619.0	26.00	36.3	25.76	120.0	26.01	38.2
-	-	-	-	28.78	14.8	-	-
-	-	-	-	30.14	7.2	-	-
33.90	19.1	-	-	34.76	369.5	35.01	87.6
-	-	-	-	-	-	36.05	40.7
44.03	0.8	-	-	44.80	4.5	-	-
55.96	107.4	-	-	55.75	659.8	-	-

Table 11

Peaks in Chromatogram of Dalton Waste Treatment Plant and Conasauga River Samples on 8% OV-17

Relative Retention Time	PLANT INFLUENT 129-11-5		CLARIFIER EFFLUENT 129-11-6		PLANT EFFLUENT 129-11-8	
	Ret. Time	Area	Ret. Time	Area	Ret. Time	Area
-	1.05	73.2	1.06	135.0	1.07	83.2
-	1.14	9.5	-	-	-	
-	1.22	16.9	1.23	33.1	1.24	18.0
-	1.35	1179.0	1.37	148.1	1.37	109.5
-	1.57	881.4	1.59	46.9	1.60	39.1
-	1.85	16.1	1.88	3.7	1.86	1.4
-	1.95	13.9	1.95	4.9	-	-
-	2.10	10.4	2.17	0.9	2.05	13.9
-	2.33	135.6	2.35	38.1	2.37	83.7
-	2.61	19.9	2.63	5.5	2.65	2.3
-	*	-	2.88	11.2	2.85	8.1
-	3.11	5.2	3.24	1.2	3.12	23.7
-	3.38	5.0	3.43	9.4	3.43	20.5
-	3.54	1.8	3.78	5.2	3.80	9.1
11	4.02	9.5	4.05	3.5	4.06	23.9
-	-	-	-	-	4.43	24.5
14	4.90	16.5	-	-	-	-
15	5.46	30.3	5.47	33.4	5.40	2.3
17	5.97	54.4	6.01	91.4	6.03	58.0
19	6.70	13390.0	6.73	692.4	6.76	385.6
22	7.90	1068.0	7.98	136.3	8.02	116.3
25	*	-	9.10	21.0	9.13	10.3
28	10.26	342.4	10.19	957.8	10.23	622.6
33	11.95	157.4	-	-	11.94	52.0
36	12.83	59.0	-	-	-	-
36	12.89	26.3	-	-	-	-
37	-	-	13.39	18.3	-	-
38	-	-	13.54	1.4	-	-
39	-	-	14.05	39.5	14.09	5.9
46	16.69	895.2	16.75	27.2	-	-
50	-	-	17.87	27.2	17.90	176.2
56	20.69	401.2	20.43	14.7	20.25	373.7
99	38.53	1036.0	38.59	125.8	38.73	74.7
137	49.57	22.4	41.39	49.5	49.58	18.9
169	61.09	940.6	61.15	379.6	61.44	481.1
191	69.05	190.0	69.07	578.4	69.24	275.4

Table 12

Possible Chlorinated Biphenyls in Dalton Waste Treatment
Plant and Conasanga River Samples

Compound	PLANT INFLUENT 129-11-5 R.R.T.	Area	CLARIFIER EFFLUENT 129-11-6 R.R.T.	Area	RETURN SLUDGE 129-11-7 R.R.T.	Area	PLANT EFFLUENT 129-11-8 R.R.T.	Area	LOOPER'S BRIDGE 129-12-9 R.R.T.	Area
3% OV-1										
2-monochloro-	-	-	14	22.1	14	8.6	14	75.8	14	2.3
2,2'-dichloro	-	-	19	190.1	19	203.7	20	271.8	19	12.9
2,4,6-trichloro-	26	13,400	26	315.0	27	332.6	27	270.3	26	17.2
6% OV-17										
2-monochloro-	-	-	10	12.7	10	66.1	10	67.9	-	-
2,2'-dichloro-	15	89.8	16	22.2	*	-	*	-	-	-
2,4-dichloro-	17	567.5	17	161.3	17	238.4	17	117.6	-	-
2,3-dichloro-	-	-	20	26.3	*	-	20	91.8	-	-
2,4,6-trichloro-	23	177.0	23	41.9	*	-	*	-	-	-
8% OV-17										
2-monochloro-	11	9.5	11	3.5	-	-	11	23.9	-	-
2,2'-dichloro-	17	54.4	17	91.4	-	-	17	58.0	-	-
2,4-dichloro-	19	13,390.0	19	692.4	-	-	19	385.6	-	-
2,3-dichloro-	22	1068.0	22	136.3	-	-	22	116.3	-	-
2,4,6-trichloro-	*	-	25	21.0	-	-	25	10.3	-	-

Table 13

Peaks in Gas Chromatograms of Laboratory Chlorinated Biphenyl Solutions on 6% OV-17

Relative Retention Time	129-19-4		129-19-1		129-19-2		129-19-3	
	Retention Time	Area	Retention Time	Area	Retention Time	Area	Retention Time	Area
4	-	-	-	-	-	-	1.03	608
5	1.27	0.5	-	-	1.12	15	1.15	-
6	1.50	0.9	1.49	0.8	1.49	0.8	-	-
7	1.68	4.7	1.67	10.2	1.67	1.8	1.69	665
8	1.87	15.5	1.88	16.2	1.86	3.2	2.08	42
11	2.54	3.7	2.53	1.6	2.39	2,285	2.56	193
12	-	-	-	-	-	-	2.85	25
14	3.26	0.7	-	-	3.17	156	3.19	8
16	-	-	-	-	3.65	591	3.66	2,603
17	4.00	1.1	4.01	0.8	4.03	565	*	-
21	4.84	2.2	4.95	1.9	4.67	11,540	4.67	16,010
26	6.04	2.3	6.17	0.6	*	-	6.16	8,240
28	*	-	6.63	0.4	6.88	2,591	-	-
32	7.43	0.3	7,53	1.4	-	-	7.32	9,242
36	8.33	0.8	8.47	4.5	8.32	1,294	8.28	16,870
39	*	-	*	-	*	-	9.03	5,623
42	-	-	-	-	9.87	1,392	9.85	10,620
30	10.47	3.0	-	-	-	-	-	-
52	12.15	3.8	12.31	16.8	12.31	801	12.53	7,994
63	-	-		-	-	-	14.64	85
65	-	-	-	-	15.02	370	15.23	2,300
69	-	-	-	-	-	-	16.15	2,825
75	17.69	1.1	17.53	0.5	-	-	-	-
83	-	-	-	-	-	-	19.51	2,636
109	-	-	-	-	-	-	25.47	2,096

Table 14

Peaks in Gas Chromatograms of Laboratory Chlorinated Biphenyl Solutions on 8% V-17

	129-19-4		129-19-1		129-25-1		129-19-2		129-19-3		NB-149	
R.R.T.	R.T.	Area	R.T.	Area	R.T.	Area	R.T.	Area	R.T.	Area	R.T.	Area
3	1.13	10.1	1.13	2.1	1.15	0.6	-	-	-	-	1.21	8.2
4	1.29	1.1	-	-	1.35	1.5	-	-	1.33	28.5	1.36	41.7
4	1.43	6.1	-	-	1.54	0.5	1.46	3.0	1.45	16.9	1.59	46.1
5	1.79	1.9	1.79	2.2	1.79	1.5	1.72	5.5	1.71	334.6	1.71	15.6
6	1.97	8.1	1.98	3.5	1.98	2.7	1.99	4.0	1.97	3.5	1.85	29.5
6	-	-	-	-	2.09	2.2	-	-	-	-	2.11	201.8
7	2.30	6.7	2.32	3.5	2.22	4.7	-	-	-	-	-	-
7	2.57	39.9	2.61	20.5	2.60	24.2	2.61	2.2	2.52	104.4	-	-
8	-	-	-	-	-	-	2.75	2.8	2.72	483.4	2.75	243.1
8	-	-	-	-	2.96	6.1	-	-	3.05	6.1	2.98	3008
9	3.29	6.0	3.35	0.9	3.31	1.6	3.24	4.2	-	-	-	-
10	*	-	-	-	3.50	1.2	-	-	*	-	3.45	31.2
11	3.99	3.4	4.01	2.1	3.93	1.1	3.91	3222	3.83	15.5	3.72	400.7
12	4.34	1.3	4.39	0.9	4.38	0.4	-	-	4.34	133.7	4.32	31.2
14	5.02	3.3	5.09	1.6	4.90	5.1	5.01	108.5	-	-	-	-
15	5.36	6.0	5.41	1.7	-	-	5.31	113.4	5.21	8.3	5.15	197.4
16	-	-	-	-	5.82	1.3	-	-	-	-	-	-
17	-	-	-	-	-	-	6.06	713.6	6.00	2115	6.05	244.5
19	6.57	15.4	-	-	*	-	6.59	885.6	6.50	156.7	6.70	258.5
21	-	-	-	-	-	-	7.58	17810	7.49	16,660	7.27	232.2
21	7.85	6.7	7.87	20	8.02	5.9	-	-	-	-	-	-
25	8.68	3.0	8.78	0.8	-	-	-	-	-	-	8.83	86.6
28	-	-	-	-	-	-	-	-	9.83	449.1	9.63	47.0
29	10.60	13.7	10.24	10.1	10.77	7.8	10.23	2814	9.95	7186	10.78	2662
32	-	-	-	-	11.26	2.9	11.25	2066	*	-	-	-
33	11.67	5.6	*		-	-	-	-	11.85	8450	-	-
37	13.08	37.2	13.30	5.2	13.29	9.1	13.20	1086	13.01	20790	13.40	125.6
40	*	-	14.16	-	14.36	9.8	*	-	14.25	5632	13.98	125.6
44	-	-	-	-	-	-	15.35	2892	15.44	9252	15.09	17.9
45	15.93	13.5	16.22	8.5	-	-	-	-	-	-	16.06	-
50	-	-	-	-	-	-	-	-	-	-	17.75	3352
56	19.88	9.8	20.22	3.3	20.08	2.4	19.93	281.8	19.55	5 294	19.83	296.8

2-monochlorobiphenyl	(11)
4-monochlorobiphenyl	(14)
2,2'-dichlorobiphenyl	(16)
2,4-dichlorobiphenyl	(19)
2,3-dichlorobiphenyl	(21)
3,3'-dichlorobiphenyl	(26)
2,4,4'-trichlorobiphenyl	(37)

The intensities vary significantly for the various compounds depending on the particular chlorination technique employed.

C. Quantitative Determination of Chlorinated Biphenyl Compounds

The quantities of the various chlorinated biphenyls present in the samples investigated were determined from the peak areas in the chromatograms. For this determination the detector was calibrated by injecting known concentrations of the various chlorinated biphenyl isomers and determining the areas under the peaks. A calibration factor for each isomer was then obtained by dividing the weight of material by the area under the peak. These calibration factors for the various isomers are given in Table 15. Calibration factors based on the standard Aroclor samples were also determined and are shown in Table 15. These factors were computed using the mean weight percent data reported by Webb and McCall [10]. With one or two exceptions the data agree reasonably well (within a factor of 3). A combination factor was selected for each isomer which is a composite result of the data in Table 15. The actual factors used are shown in the last column of Table 15.

Table 15

Calibration Factors for the Electron Capture Detector For Various Polychlorinated Biphenyl Isomers
(in gm/unit area)

R.R.T.	Compound	6% OV-17 Run 1	6% OV-17 Run 2	8% OV-17	Based on Aroclor 1221	Based on Aroclor 1242	Based on Aroclor 1248	Calibration Factor Used in Analysis
11*	2-monochloro-	1.22×10^{-12}	0.94×10^{-12}	—	3.47×10^{-13}	—	—	3.47×10^{-13}
14	4-monochloro-	5.07×10^{-13}	3.21×10^{-12}	2.80×10^{-13}	—	—	—	2.80×10^{-13}
16	2,2'-dichloro-	1.08×10^{-13}	1.02×10^{-13}	1.02×10^{-13}	2.69×10^{-13}	3.07×10^{-13}	—	1.04×10^{-13}
19	2,4-dichloro-	1.50×10^{-14}	1.22×10^{-14}	0.99×10^{-14}	—	—	—	1.26×10^{-14}
21	2,3-dichloro-	—	1.19×10^{-14}	0.81×10^{-14}	—	—	0.69×10^{-14}	1.00×10^{-14}
19	2,5-dichloro-	—	6.50×10^{-15}	4.80×10^{-15}	—	—	—	5.65×10^{-15}
—	2,6-dichloro-	—	2.09×10^{-14}	1.93×10^{-14}	—	—	—	2.01×10^{-14}
—	3,3'-dichloro-	—	2.06×10^{-13}	0.60×10^{-13}	—	—	—	1.33×10^{-13}
—	3,4-dichloro-	—	3.62×10^{-14}	2.05×10^{-14}	—	—	—	2.84×10^{-14}
28*	4,4'-dichloro-	3.76×10^{-13}	—	4.68×10^{-14}	—	—	6.31×10^{-15}	6.31×10^{-15}
37	2,4,4'-trichloro-	—	7.80×10^{-15}	5.40×10^{-15}	—	16.8×10^{-15}	3.30×10^{-15}	6.60×10^{-15}
—	2,4,6-trichloro-	—	2.90×10^{-15}	1.47×10^{-15}	—	—	—	2.19×10^{-15}
40	—	—	—	—	—	1.83×10^{-14}	0.88×10^{-14}	1.36×10^{-14}
47	—	—	—	—	—	5.75×10^{-15}	4.46×10^{-15}	5.11×10^{-15}
54	—	—	—	—	—	1.34×10^{-14}	0.40×10^{-14}	0.87×10^{-14}
58	—	—	—	—	—	1.22×10^{-14}	0.40×10^{-14}	0.81×10^{-14}
70	—	—	—	—	—	3.22×10^{-14}	2.96×10^{-15} ⊕	3.22×10^{-14}

* Samples of model compounds showed significant peaks in addition to peak for the principal compound

⊕ Some overlap with a second peak may have given an unusually large error in this factor.

The concentration of the various chlorinated biphenyl isomers in the samples analyzed was determined by the following equation:

$$\text{Conc.(ppb)} = \frac{\text{Area x Calibration Factor}}{\text{Sample Volume x Concentration Factor x } 10^6}$$

The area was determined directly by the gas chromatograph, the sample volume varied from 2.2 to 2.4 microliters, and the concentration factor was 200 for samples 129-1-1 to 129-12-9 (1 liter concentrated in 5 ml). If possible all calculations were based on area obtained from runs on the 8% OV-17 column (data in the lower sections of Tables 8 and 12). In a few cases areas from runs on 3% OV-1 or 6% OV-17 were used (Samples 129-11-7 and 129-12-9 and for 2,4,6- trichlorobiphenyl in all samples.) Results of the analyses are given in Table 16.

Similar results for the laboratory chlorinated samples are given in Table 17. The calculations for these samples were based on the 8% OV-17 chromatograms and the concentration factor was 11/3500.

V. Discussion

Based on the data in Tables 16 and 17 a number of important conclusions can be drawn about chlorination of biphenyl. First, as indicated by samples 129-10-1, 129-10-2, 129-10-3, and 129-10-4, only very small quantities of chlorinated biphenyl isomers are present in the Dalton water supplies. The compounds that can be detected are at the very limits of detectable of the techniques used in this study.

A second important conclusion is that the chlorination procedure used at the Dalton waste treatment plant does not produce large quantities of chlorinated biphenyl. Sample 129-11-6 was taken from the clarifier effluent

Table 16

Concentration of Various Chlorinated Biphenyl Isomers
in Dalton Water and Wastewater Samples
(in parts-per-billion)

R.R.T. Webb & McCall	Compound	FINISH WATER(C) 129-10-1 2.2 ul	RAW WATER(C) 129-10-2 2.4 ul	FINISH WATER(M) 129-10-3 2.3 ul	RAW WATER(M) 129-10-4 2.4 ul	PLANT INFLUENT 129-11-5 2.2 ul	CLARIFIER EFFLUENT 129-11-6 2.4. ul	RETURN SLUDGE 129-11-7 2.4 ul	PLANT EFFLUENT 129-11-8 2.4 ul	LOOPER'S BRIDGE 129-12-9 2.4 ul
11	2-monochloro-	N.D.	N.D.	N.D.	N.D.	7.5	2.8	6.2	17.2	1.7
14	4-monochloro-	N.D.	< 1	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
16	2,2'-dichloro-	N.D.	< 1	N.D.	N.D.	12.9	19.8	*	12.6	2.8
19	2,4-dichloro-	N.D.	N.D.	N.D.	N.D.	383	18.2	*	10.1	N.D.
21	2,3-dichloro-	< 1	< 1	< 1	< 1	24.3	2.8	*	2.4	N.D.
37	2,4,4'-trichloro-	< 1	< 1	< 1	< 1	N.D.	N.D.	N.D.	N.D.	N.D.
	2,4,6-trichloro-	N.D.	N.D.	N.D.	N.D.	61.1	1.4	1.5	1.2	< 1

N.D. = not detected

* = peak detected but could not be quantitated

Table 17

Concentration of Various Chlorinated Biphenyl Isomers
in Laboratory Chlorinated Samples

(in parts-per-billion)

R.R.T. Webb & McCall	Compound	129-19-4 2.4 ul	129-19-1 2.4 ul	129-25-1 2.8 ul	129-19-2 2.4 ul	129-19-3 2.4 ul	Reported in Ref. 6	NB-149 2.4 ul
11	2-monochloro-	1.5	<1	<1	1500	7.0	180	182
14	4-monochloro-	1.2	<1	2.0	40	3.0	80	72
16	2,2'-dichloro-	N.D.	N.D.	<1	97	288	80	33
19	2,4-dichloro-	<1	N.D.	*	15	2 .6	—	4.3
21	2,3-dichloro-	N.D.	N.D.	N.D.	230	220	370	3.0
—	3,3'-dichloro-	N.D.	N.D.	N.D.	N.D.	78	—	8.2
28	4,4'-dichloro-	<1	<1	<1	23	59	500	22
37	2,4,4'-trichloro-	<1	<1	<1	9.4	180	—	1.1

N.D. = not detected

* = detected but could not be quantitated

and Sample 129-11-8 from the contact chlorination effluent. A comparison of these two samples (Table 16) indicates that some increase in 2-monochlorobiphenyl may occur (2.8 to 17.2 ppb) but the concentrations of other chlorinated biphenyl isomers decrease slightly, although the decrease is probably within the experimental error. The concentrations of 2,4- dichloro-, 2,3-dichloro- and 2,4,6,-trichloro appears to be significantly reduced in the clarifier effluent compared to the plant influent. Some biodegradation and/or adsorption of these isomers on the sludge may be responsible for this reduction.

The conclusion that polychlorinated biphenyls are not produced by the usual chlorination process is substantiated by results from the laboratory chlorination studies. A comparison of samples 129-19-4 with 129-19-1 and 129-25-1 clearly indicates that biphenyl was not chlorinated under the conditions designed to simulate waste treatment plant conditions. On the other hand, samples 129-19-2 and 129-19-3 show that substantial chlorination occurs at lower pH and with higher levels of chlorine treatment. Chlorination under these more stringent conditions has previously been reported by Carlson whose data are shown in column 8 of Table 17.

The most puzzling finding of the present work is that chlorinated biphenyl isomers are present in the influent to the Dalton waste treatment plant. These compounds could come from a variety of sources. Leakage from transformers or capacitators that enters the city sewer system may account for some of these compounds.

Certain carpet processing operations may also be responsible for part of the chlorinated biphenyl present in the influent. Occasionally, a carpet will be dyed to too deep a shade and the color must be reduced by a "stripping" process. Sodium hydrosulfite is usually used for this purpose, but in some stripping operations sodium chlorite, formic acid

and biphenyl based carriers may be used. This type of stripping operation was simulated in the laboratory and the resulting bath analyzed for chlorinated biphenyls. Results for this sample, NB-149, are shown in the last column of Table 17. It is clear that chlorinated biphenyls are produced under these conditions.

In concluding, some comments about the validity of the current results should be made. First, identification of chlorinated biphenyls was based on coincidence of retention times on at least two different gas chromatography columns. This does not provide unequivocal identification. The identifications are somewhat further substantiated by the appearance of peaks with comparable retention times when samples of biphenyl were chlorinated in the laboratory. An attempt to further confirm the peak identification using gas chromatography and mass spectrometry is underway.

Second, quantitation of identified peaks can be subject to many errors. In the present work the same samples were analyzed more than once on different columns and using different techniques for calibration. The results for three different analyses of one sample, 129-12-3, are shown in Table 18. These results give, at least some indication, of the variation in the quantitation of chlorinated biphenyls in these samples. The large difference in the value for 2-monochlorobiphenyl in Run 1 is due to interference by another compound on the 6% OV-17 column.

Table 18

Three Analyses of Sample 129-19-3
(in parts-per-billion)

R.R.T. W.& M.	Compound	Run 1	Run 2	Run 3
11	2-monochlorobiphenyl	253	20	7
14	4-monochlorobiphenyl	10	3	3
16	2,2'-dichlorobiphenyl	341	283	288
19	2,4-dichlorobiphenyl	—	2	3
21	2,3-dichlorobiphenyl	210	178	220
	3,3'-dichlorobiphenyl	-	38	78
28	4,4'-dichlorobiphenyl	108	—	59
37	2,4,4'-trichlorobiphenyl	221	—	180

The results of this study suggest that minor changes in carpet processing, particularly in the stripping and scouring operations, should be considered to reduce the possibility of chlorination of biphenyl.

V. Conclusions

Based on the results of this study a number of conclusions are possible:

1. There is no evidence from analysis of gas chromatograms of samples collected at the Dalton waste treatment plant or samples produced by laboratory chlorination of biphenyl that polychlorinated biphenyl (PCB's) are produced under conditions that usually exist in treating carpet dye wastewater. There is some evidence that small quantities of a monochlorobiphenyl may be produced in waste treatment plant chlorination.

2. Chlorinated biphenyls are present in the influent to the Dalton waste treatment plant. These compounds are not present in either of the two city water supplies and their origin is unknown at the present time.

3. Laboratory chlorination experiments indicate that some chlorinated biphenyls may be produced when polyester carpet is stripped with chlorine containing stripping agents under the usual highly acidic conditions. Stripping of carpet with these agents should be discouraged.

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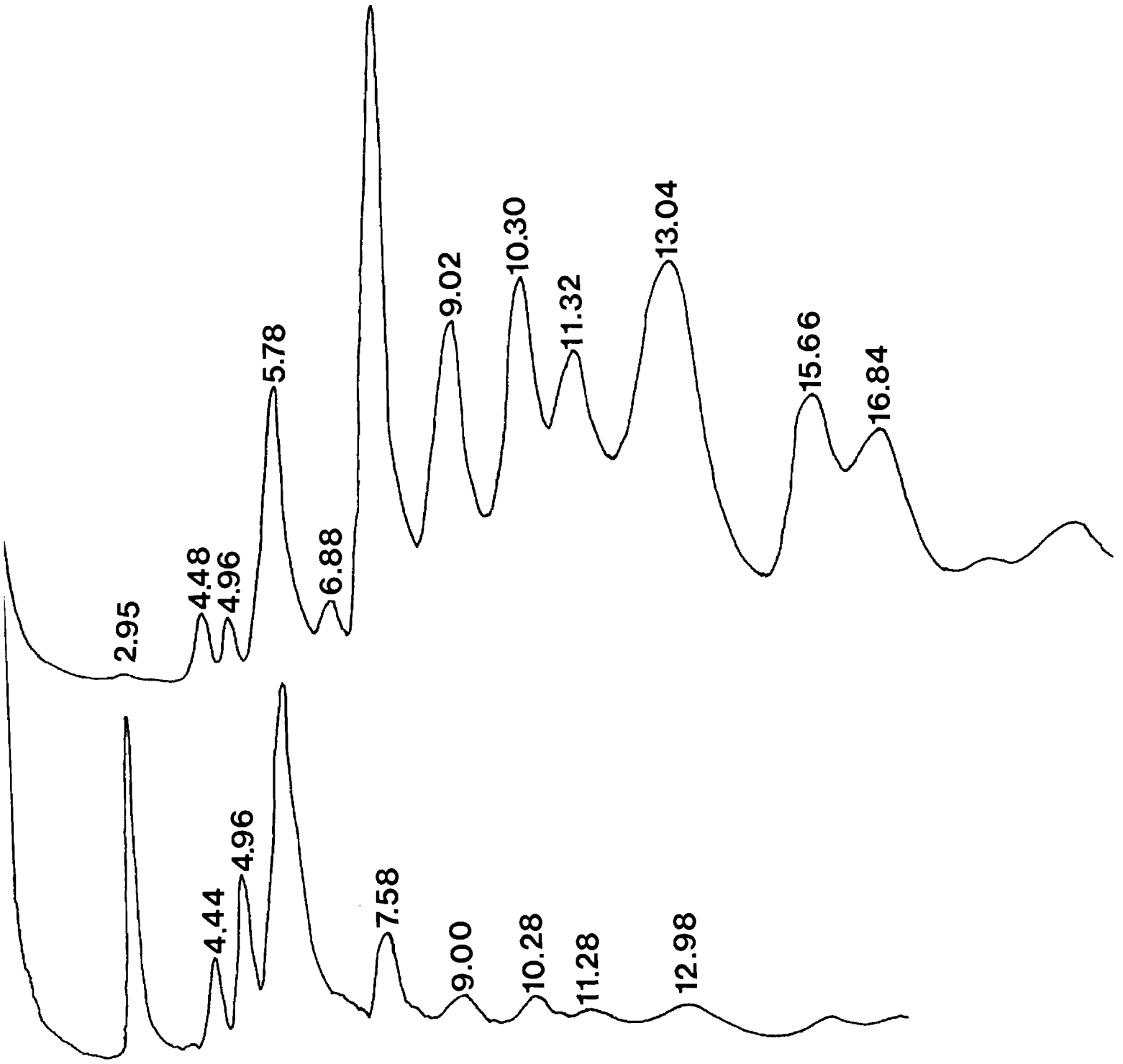

FIGURE 1--GAS CHROMATOGRAMS OF AROCLOR 1242 (TOP) AND AROCLOR 1221 (BOTTOM) ON 6% OV-17.

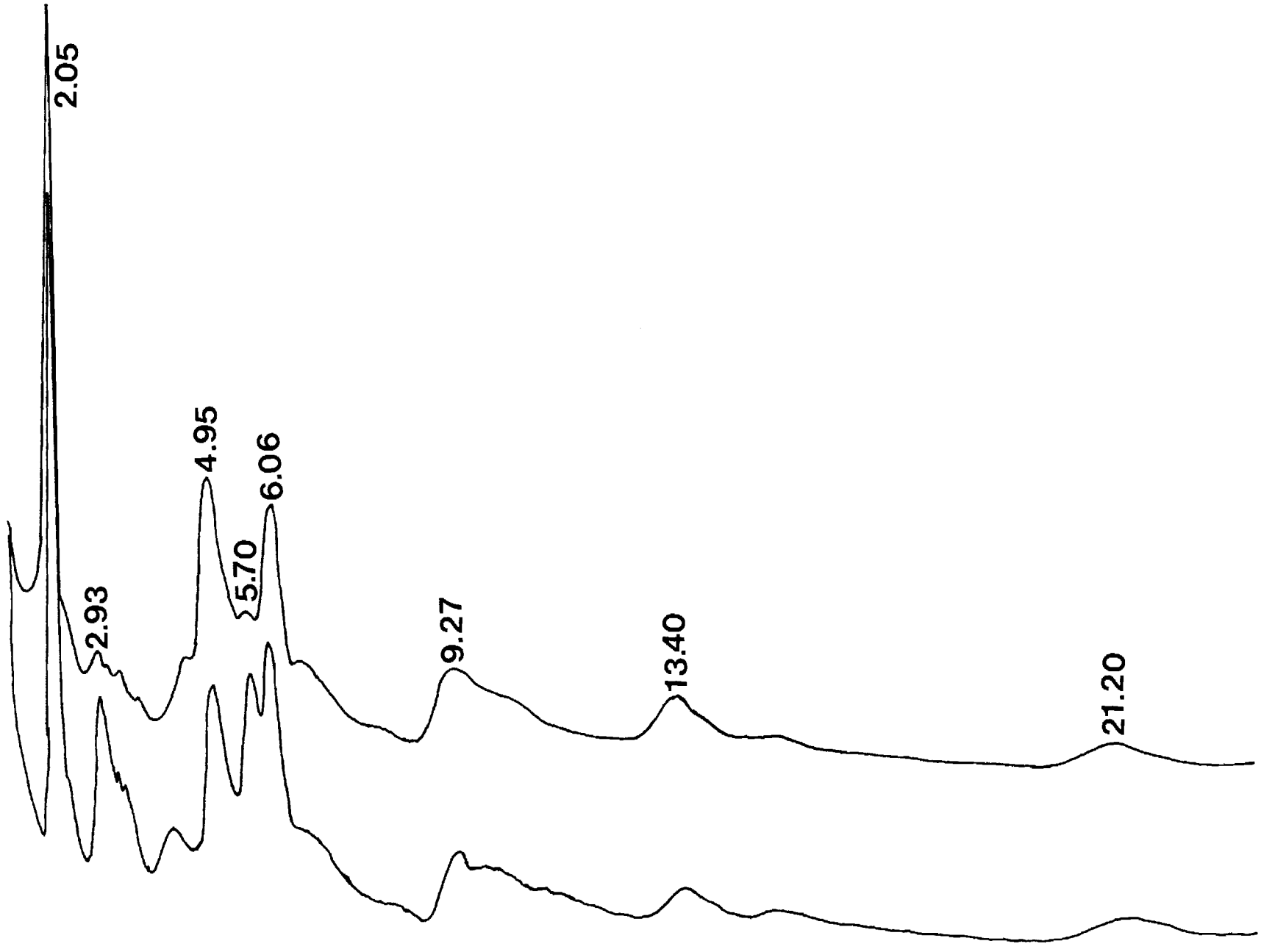

FIGURE 2--GAS CHROMATOGRAMS OF SAMPLES 129-11-6 (TOP) AND 129-11-8 (BOTTOM).

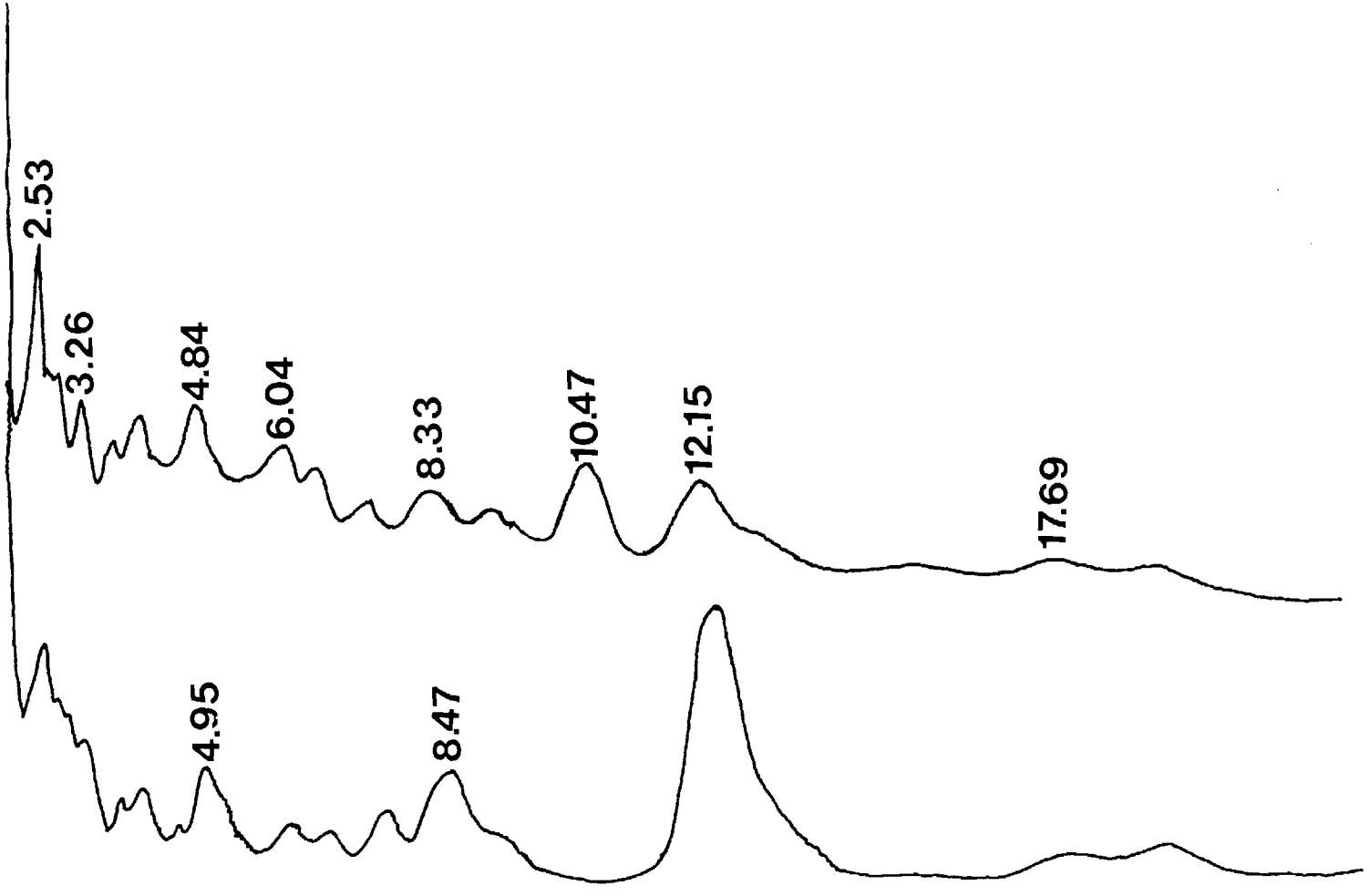

FIGURE 3--GAS CHROMATOGRAMS OF SAMPLE 129-19-4 (TOP) AND SAMPLE 129-19-1 (BOTTOM) ON 6% OV-17 (PP'DDE = 23.31).

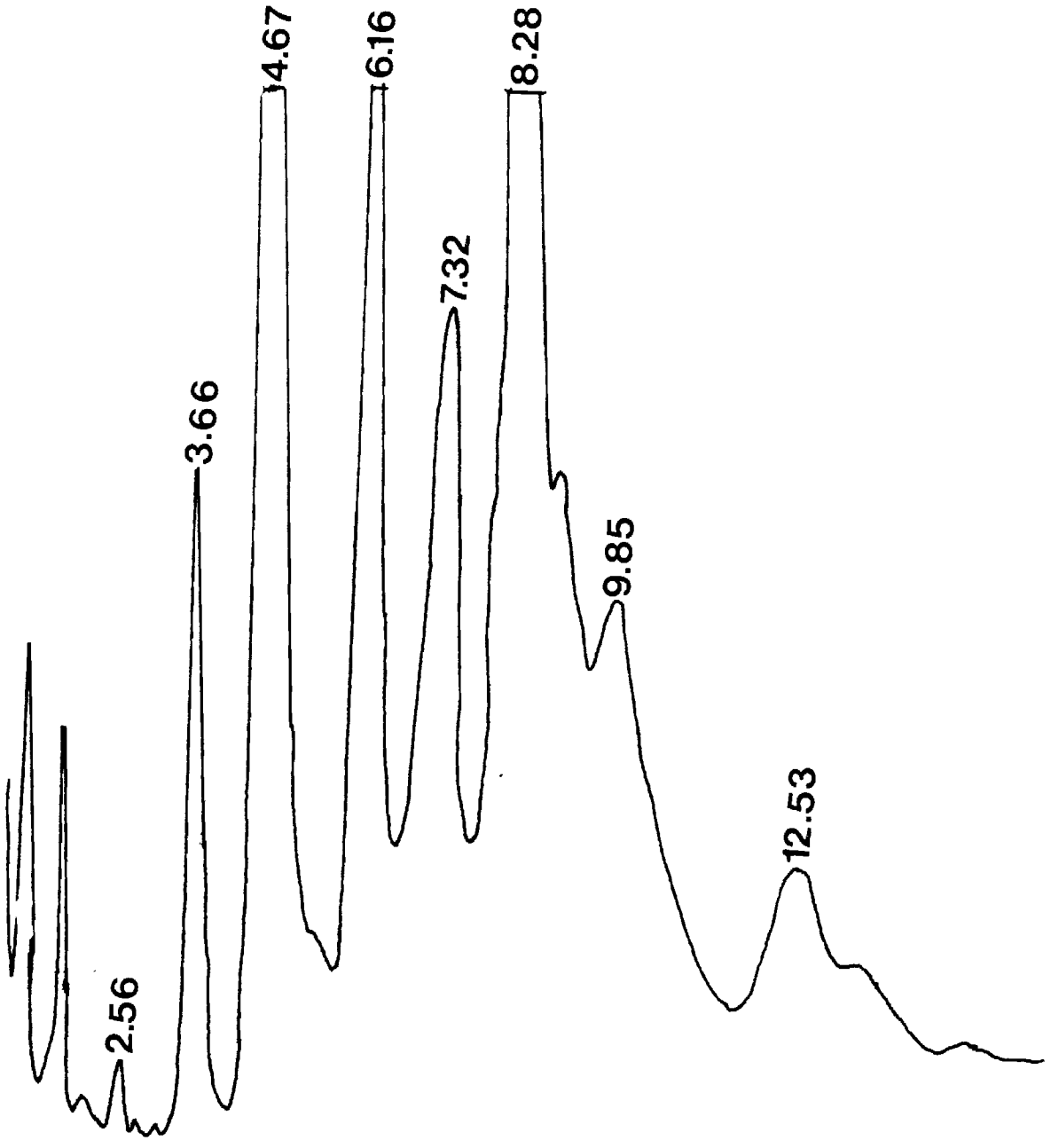

FIGURE 4--GAS CHROMATOGRAM OF SAMPLE 129-19-3 ON 6% OV-17.

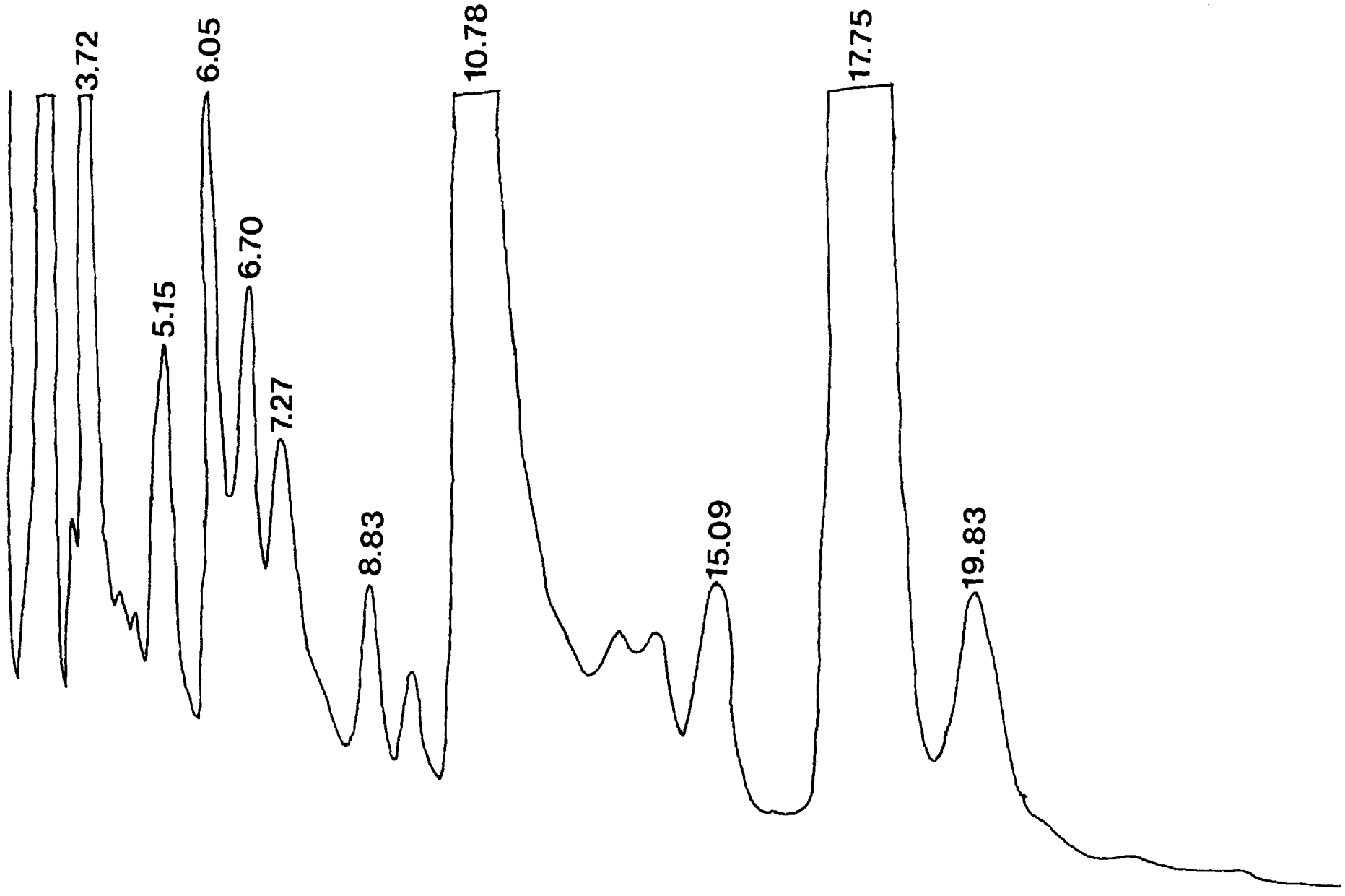

FIGURE 5--GAS CHROMATOGRAM OF SAMPLE NB-149 ON 8% OV-17.

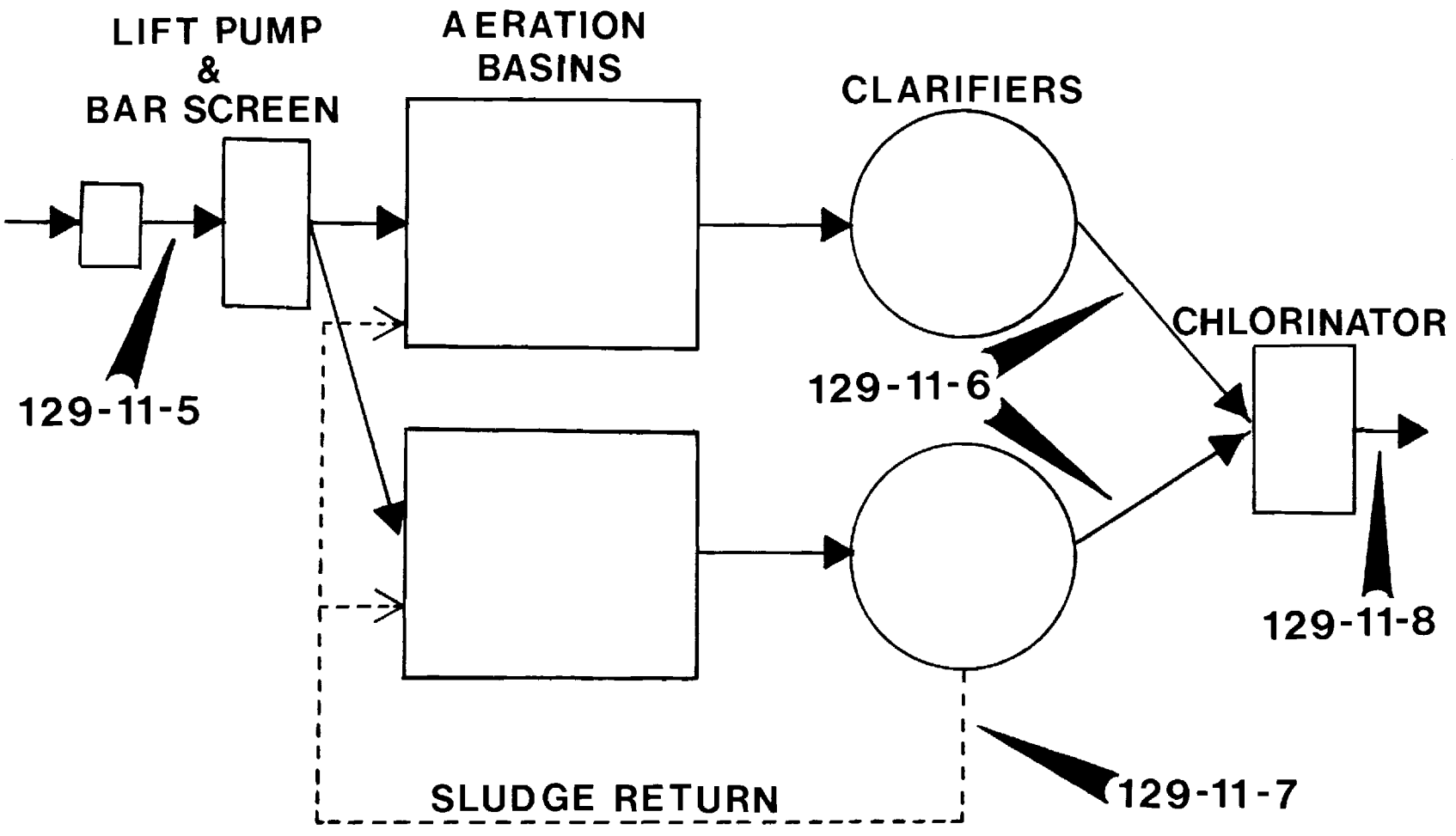

FIGURE 6 -- SAMPLING POINTS AT THE DALTON WASTE TREATMENT PLANT